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Physical properties of the cubic spinel $LiMn_2O_4$

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ABSTRACT

We have performed an ab initio study of structural, electronic, magnetic, vibrational and thermal properties of the cubic spinel $LiMn_2O_4$ by employing the density functional theory, the linear-response formalism, and the plane-wave pseudopotential method. An analysis of the electronic structure with the help of electronic density of states shows that the density of states at the Fermi level ($N(E_F)$) is found to be governed by the Mn 3d electrons with some contributions from the 2p states of O atoms. It is important to note that the contribution of Mn 3d states to $N(E_F)$ is as much as 85%. From our phonon calculations, we have obtained that the main contribution to phonon density of states (below 250 cm^{-1}) comes from the coupled motion of Mn and O atoms while phonon modes between 250 cm^{-1} and 375 cm^{-1} are characterized by the vibrations of all the three types of atoms. The contribution from Li increases rapidly at higher frequency (above 375 cm^{-1}) due to the light mass of this atom. Finally, the specific heat and the Debye temperature at 300 K are calculated to be 249.29 J/mol K and 820.80 K respectively.

1. Introduction

In recent years, great attention has been paid to lithiated transition-metal oxides such as $LiCoO_2$, $LiNiO_2$ and $LiMn_2O_4$ due to their industrial applications particularly in recharge lithium-ion batteries [1–11]. These lithiated transition-metal oxides are used as the cathode side of lithium-ion batteries where Li has been extracted and stored during the charge–discharge cycle of the battery. Among these cathode materials, $LiMn_2O_4$ has highly alluring properties, such as low cost, non-toxicity, environmental compatibility, safety and a good thermal stability [7–11]. It is well known that the electrochemical performance of the cathode is vigorously influenced by the physical properties of the materials [12–14]. It is therefore important to thoroughly investigate its structural, magnetic, electronic and vibrational properties. The lattice constant, internal parameter, bulk modulus and magnetic moment have been measured by several experimental groups [15–19]. The dielectric and electronic properties were determined by analyzing the low-loss region of the electron energy-loss spectroscopy (EELS) spectrum in a transmission electron microscope [20,21]. Raman [22,23] and infrared (IR) [24,25] spectroscopies have been used to measure the zone-center phonon modes. On the theoretical side, Mishra and Ceder have studied the stability of lithium-manganese oxides using density functional theory in the local density and generalized gradient approximation [26]. The ab initio full potential linear-muffin-tin orbital (LMTO) method has been used to investigate the electronic properties of the cubic spinel $LiMn_2O_4$ [27]. In this calculation the exchange–correlation potential was treated in both the local-spin-density approximation (LSDA) and the generalized gradient approximation (GGA). Following this theoretical work, molecular dynamics (MD) simulations [28] have been used to investigate the local structural disorder in $LiMn_2O_4$. In addition to this MD study, the structural anddynamical properties of spinel $LiMn_2O_4$ have been studied from density functional theory-based ab initio MD simulations [29]. Ab initio simulations of the electron-energy-loss near-edge structures at the Li K edge in Li, Li_2O and $LiMn_2O_4$ have been made using density functional theory within the GGA [30]. The phonon dispersion relations and density of states of this material have been studied using the density functional perturbation theory (DFPT) within the GGA [31]. The geometric structures of $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ have been optimized and the corresponding electronic structures have been obtained by the density functional theory plane-wave pseudopotential method [32]. Singh and co-workers have studied the electronic structure of pristine and doped $LiMn_2O_4$ using the GGA and GGA with Hubbard U correction (GGA+U) [33]. Although $LiMn_2O_4$ crystallizes with a cubic spinel structure and belongs to the $Fd\bar{3}m$ (O_h^7) space group, the orthorhombic phase of this material has been reported in the experimental work of Kodama and coworkers due

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to lattice distortions that occur below 260 K [34]. Thus, the electronic structure of orthorhombic $LiMn_2O_4$ has been calculated using the GGA+U method [35]. Espinosa-Magana and coworkers [20,21] have used the GGA method to obtain the structural and electronic properties of the cubic spinel $LiMn_2O_4$. Comparison of electronic property and structural stability of $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$ has been made in the GGA work of Shu and coworkers [36]. The structural changes and voltages of $LiMn_2O_4$ spinel as a function of lithium content have been investigated with the GGA as well as the GGA+U method [37]. Recently, constrained density functional theory at the GGA+U within the Blue Moon ensemble has been applied to simulate aqueous dissolution of the $LiMn_2O_4$ spinel [38].

Although the electronic and vibrational properties of $LiMn_2O_4$ have been studied, the thermal properties of this material are not well reported yet. However, understanding of the thermodynamic properties of materials is of fundamental importance in solid state physics because they are necessary to understand stability, structural evolution, and other behaviors of materials under synthesis, processing, and operating conditions. Moreover, the tender knowledge of the thermal properties of crystals used in lithium ion batteries is a main issue for developing the active materials and complete cells, regarding particularly electrochemical performance, lifetime, and safety aspects [39–41]. Furthermore, the heat generated in an operating battery is usually approximated by the sum of reversible and irreversible heat. We have to mention that the change of entropy produces the reversible heat [39–41].

In this work, an ab initio pseudopotential method within the spin-polarized gradient approximation (σ-GGA) has been used to investigate the structural, magnetic, and electronic properties of the cubic spinel $LiMn_2O_4$. We have compared our structural and magnetic results with calculations and experimental data available in the literature. The electronic structure and electronic density of states for this material are presented and discussed in detail. We have further carried out ab initio linear response (DFPT) calculations of the lattice dynamics and a discussion on the polarization characteristics of zone-center phonon modes. In addition to structural, electronic and vibrational properties, the density functional perturbation theory with quasi-harmonic approximation (QHA) [42] is applied to determine thermal quantities such as the internal energy (E), Helmholtz free energy, constant-volume specific heat, entropy and Debye temperature.

2. Method

The cubic spinel $LiMn_2O_4$ contains fourteen atoms per unit cell: two lithium, four manganese and eight oxygen atoms. The calculations were carried out in the framework of the density functional theory with the electronic structure package QUANTUM-ESPRESSO [43]. The cubic symmetry with point-group O_h^7 and space group $Fd\bar{3}m$ was invoked in all calculations. Ultrasoft pseudopotentials for Li, Mn and O were generated by using the VANDERBILT code [44]. As the 3d electrons in the transition-metal atom Mn are incompletely filled, spin-density approximation [45] was employed within the Perdew–Burke–Ernzerhof (PBE) form [46] of the generalized gradient (σ-GGA) scheme. The wave functions are expanded in plane waves, with the energy cutoff of 60 Ry and the electronic charge density is expanded in a basis cut off up to 240 Ry. Self-consistent solutions of the Kohn–Sham equations [47] were obtained by employing a set of Monkhorst–Pack special **k** points [48] within the irreducible part of the Brillouin zone (IBZ). For geometry optimization calculations, the Brillouin zone integration was performed by using the $8\times8\times8$ Monkhorst–Pack **k**-points grid [48]. The structure in this work was fully relaxed using force as well as stress minimization schemes. A criterion of at least 0.01 meV/atom was placed on the self-consistent convergence of the total energy. The Brillouin zone integration was performed with a Gaussian broadening of 0.02 Ry. After geometry optimization calculations, the electronic structure and the electronic density of states were calculated with $(24\times24\times24)$ Monkhorst–Pack [48] **k**-point mesh.

We have used $(8\times8\times8)$ **q**-point mesh for the sampling of the IBZ for phonon calculations in the cubic spinel $LiMn_2O_4$. The phonon frequencies and atomic displacements were subsequently obtained using the linear response method [43], which avoids the use of supercells and allows the calculation of the dynamical matrix at arbitrary **q** vectors. The eigenfrequencies and eigenvectors of lattice vibrations are calculated within the framework of self-consistent density functional perturbation theory (DFPT) [43]. A static linear response of the valence electrons was considered in terms of the variation of the external potential corresponding to periodic displacements of the atoms in the unit-cell. The screening of the electronic system in response to the displacement of the atoms was taken into account in a self-consistent manner. In order to obtain full phonon spectrum, we evaluated 10 dynamical matrices on a $(4\times4\times4)$ grid in **q** for the cubic spinel $LiMn_2O_4$. These dynamical matrices were Fourier transformed to obtain the full phonon spectrum and density of states. We estimate that the phonon frequencies are accurate within 0.1 THz for the present choice of the kinetic energy cutoff and the special **k** points.

In addition to vibrational properties, we have also investigated phonon influence on the thermodynamic properties of $LiMn_2O_4$ using QHA. As is known, the first-principles calculations are limited to $T=0$ K and thermodynamic properties of $LiMn_2O_4$ can be obtained in detail by its phonon properties. Thermodynamic properties of solids can be described by the quasi-harmonic approximation [42]. Using the phonon frequencies and DOS, the phonon contribution to internal energy (E), Helmholtz free energy (F), constant-volume specific heat (C_V) along with entropy are calculated by applying the following relations:

$$E=\frac{3nN\hbar}{2}\int_0^\infty \omega\coth\left(\frac{\hbar\omega}{2k_BT}\right)F(\omega)\,d\omega \tag{1}$$

$$F=3nNk_BT\int_0^\infty \ln\left[2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right]F(\omega)\,d\omega \tag{2}$$

$$S=3nNk_B\int_0^\infty \left(\frac{\hbar\omega}{2k_BT}\coth\left(\frac{\hbar\omega}{2k_BT}\right)-\ln\left[2\sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right]\right)F(\omega)\,d\omega \tag{3}$$

where n is the number of atoms in the unit cell, N is the number of unit cells, k_B is Boltzmann's constant, $\hbar$ is Planck's constant, T is the temperature and $F(\omega)$ is the phonon density of states.

3. Results

3.1. Structural and electronic properties

$LiMn_2O_4$ crystallizes in the cubic spinel structure, illustrated in Fig. 1(a), with space group (227) $Fd\bar{3}m$. The primitive unit cell of this structure contains fourteen atoms: two lithium, four manganese and eight oxygen atoms. Lithium atoms occupy the 8a tetrahedral sites (0.125, 0.125, 0.125), manganese atoms occupy the 16d octahedral sites (0.5, 0.5, 0.5), and oxygen atoms generate a cage and occupy the 32e sites (x, x, x). Thus the spinel structure is described by the lattice parameter a and the anion internal parameter x.

We determined the equilibrium values of the lattice parameter a and the internal parameter x by minimizing the crystal total energy calculated for different values of a. The total energy results,